Silylformylation - Fluoride-Assisted Aryl Migration of Acetylenic Derivatives: a Versatile Approach to the Synthesis of Polyfunctionalised Compounds

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Polyfunctionalised aldehydes and dihydropyrans are prepared from easily available functionalised 1-alkynes through a silylformylation-aryl migration two-steps sequence. The silylformylation process is performed under mild experimental conditions and affords the corresponding β-silylalkenals with high yields. The fluoride-promoted migration step occurs instantaneously with quantitative conversion. The chemo-, regio- and stereoselectivity can be modulated according to the nature and the position of the functional group on the acetylene precursors. When a good leaving group is present in the ω position of the aliphatic chain of the alkyne a cyclisation product is obtained, while α,β-unsaturated aldehydes are generated from propargylic tosylamides.

Introduction

The reactions of carbon-silicon bond formation are of great importance and widely used in organic synthesis. Among a variety of methods developed for such transformations, transition metal promoted

silylations[1] provide useful routes to organo silicon compounds, now receiving much attention owing to their low cost, low toxicity, generality, selectivity and ease of handling. For instance, the rhodium mediated silylformylation reaction of acetylenic substrates has been studying intensively for more than ten years[2] since it generates β-silylalkenals, polyfunctionalised compounds that can be submitted to Peterson olefination,[3] Nazarov and Trost type annulations,[4] isomerization of the double bond, reduction and Wittig transformation of the carbonylic group.[5]

Recently, taking advantage of the high chemical affinity (BDE Si-F= 135 Kcal) between silicon and fluorine,[6] we were able to convert 2-(dimethylphenylsilylmethylene)hexanal into the corresponding 2-benzylhexanal through the aromatic ring migration from the dimethylphenylsilyl moiety to the adjacent carbon atom of the β-silylalkenal (Scheme 1, step 2).[7] The two steps sequence of silylformylation-phenyl migration was successfully applied to several terminal acetylenes and arylsilanes yielding 2-arylmethylaldehydes, useful building blocks for organic chemistry[8] and important industrial products.[9] Here we report the extension of this tandem process to variously functionalised acetylenic substrates and the preparation of different classes of compounds (linear, cyclic, unsaturated) according to the nature and the position of the functional group on the aliphatic chain of the alkyne.

Results and discussion

An important condition for the synthetic utility of the two steps approach centred on such a Si-C migration is the ready access to the requisite (*Z*)-β-silylalkenals. Actually, silylformylations of terminal acetylenes can be easily performed at room temperature in a stainless steel autoclave. In a typical run, a toluene solution of equimolar amount of silane and alkyne and a catalytic quantity of $Rh_4(CO)_{12}$ was introduced in the autoclave, the reactor was pressurized with carbon monoxide and stirred for the required time (Tables 1-2, step 1).

As expected, the reactions proceeded with complete regioselectivity since the silicon is usually introduced onto the terminal position of the acetylenes. The pressure of carbon monoxide was chosen according to the steric hindrance of both the unsaturated substrates and the silanes. The corresponding (*Z*)-β-silylalkenals were obtained with high yields regardless of the electronic and steric requirements of both the alkynes and the silanes (Table 1, 2, step 1), confirming the trend we previously observed.[7b] It is well known that the silylformylation reaction can tolerate many functional groups on the alkynes. Indeed, when α, β and ω substituted acetylenes were reacted with Me_2PhSiH, chosen as model reagent, the presence of double or triple bonds, nitrile, halogens, tosylate, hydroxyl or amido groups did not markedly affect the reactions that yielded the expected products quantitatively in most cases (Tables 1-2, Scheme 3, step 1). It is noteworthy that when an acetylene bearing a free amino group was reacted with the silane it was not possible to isolate the β-silylalkenal although a complete conversion of the reagents was observed with concomitant formation of some unidentified materials. Moreover, small amounts of by-products of double silylation were detected when 1,7-octadiyne was used even if in this case the reaction was carried out with excess alkyne and under high CO pressure (Table 1, entry 5).

With the easy access to the (*Z*)-β-silylalkenals in hand, we turned to the TBAF promoted migration step (tables 1, 2, step 2). The reactions were performed at room temperature adding 2 mmol of aldehyde to 5 mL of TBAF (1 M in THF solution) and hydrolysing the resulting solution immediately after with water. The 1,2 rearrangement of the aromatic ring occurred smoothly with complete retention of the original configuration of the Ar group (Table 1, entries 1-4, step 2). Instead, the chemical features of the functional group situated on the acetylenic substrate had a great influence on the proceeding of the reactions. Unsaturated moieties (C=C, C≡C), a nitrile or hydroxyl group in the ω position of the alkynes were not involved in the migration step but were directly transferred to the saturated aldehydic products (Table 1, entries 5-8, step 2). On the contrary, the presence and the position of a leaving group on the aliphatic chain of the acetylenes had a dramatic effect on the chemo- and regioselectivity of the process.

When a halide or a tosyl substituent was situated at the end of the hydrocarbon chain, exo tet ring closure reactions took place with the formation of three-, five- and six-membered ring products, all favoured according to Baldwin rules (Table 2, step 2).[12] Cycloalkanecarbaldehydes **7**, **11, 13, 14** (Table 2, entries 1, 5-8, step 2) and 5-benzyl-3,4-dihydro-2H-pyran **8** (Table 2, entries 2-4, step 2) were obtained as major products. In particular, aldehydes **7**, **11, 13, 14** were generated by intramolecular *C*-alkylation of the carbanion **15** formed after the fluoride addition to the silicon atom and subsequent phenyl migration (Scheme 2). In the cases of α-branched acetylenes **5g-h** the cyclisation reactions took place with good diastereoselectivity, **(*Z*)-13** and **(*Z*)-14** being formed as major isomers (Table 2, entries 7-8, step 2). The benzyldihydropyran **8** (Table 2, entries 2-4, step 2) was obtained by kinetically favoured intramolecular *O*-alkylation of the enolate form of **15** (Scheme 2). A complete chemoselectivity towards **8** was observed in the presence of an excellent leaving group such as tosylate (Table 2, entry 4, step 2), while the reaction of ω-chlorinated **(*Z*)-6b** and ω-brominated β-silylalkenales **(*Z*)-6c** involved the formation of relevant amounts of by-products (Table 2, entries 2, 3, step 2). In the case of aldehyde **(*Z*)-6b** together with the cyclisation products **8**, the TBAF mediated reactions yielded the linear 1-benzylaldehyde **9** probably due to the poor leaving group properties of chlorine (Table 2, entry 2, step 2). Analogously when **(*Z*)-6e** was reacted with TBAF the formation of the chloroaldehyde **12** was detected (Table 2, entry 5, step 2). The presence of bromine in the ω position induced the formation of carbacyclic aldehyde **10**, that can be ascribed to the carbanion **16**, generated by Brook rearrangement[13] of **15** (Scheme 2).

The obtained results prompted us to extend our investigation to the reactivity of propargyl derivatives (Scheme 2, n = 0) characterised by a good leaving group such as acetate or tosylamide in the α position with respect to the triple bond. As described in Scheme 3, while the reactions of propargylamine **5k** protected as NHBOC yielded the "normal" rearrangement product **18** exclusively, the TBAF treatment of the β-silylalkenals derived from alkynes **5i, j** determined the formation of α,β-unsaturated aldehydes **17**.

The observed behaviour is in agreement with the mechanism depicted in Scheme 4 and can be easily explained considering that in this case the carbanion generated after the phenyl migration induces the elimination of OAc and *p*TsNH and the consequent double bond formation (Scheme 4). 2-Benzyl-3-methylpentenal **17** was obtained with good yields (59-62%, pure product) but poor stereoselectivity, as could be expected from the very similar steric requirements of the methyl and ethyl substituents. On the contrary, the β-silylalkenal **20** derived form propargylamide **19** afforded exclusively the stereoisomer **21** characterised by the bulky *t*butyl substituent in trans to the carbonyl moiety (Scheme 5).

Conclusions

In conclusion in the tandem process silylformylation-fluoride promoted Si→C rearrangement, the chemo-, regio- and stereoselectivity of the desilylation reaction turned out to be closely related to the nature and the position of the functional group present on the silylformylation product. The ready access to functionalised β-silylalkenals through silylformylation reactions enhances the versatility of the protocol that can successfully employed to the preparation of polyfunctionalised aldehydes and pyrans, useful building blocks for organic chemistry.

Experimental section

General procedure for the Rhodium-catalyzed silylformylation of 1-alkynes with aryldimethylsilanes. Carbonylation reactions were run in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 3 mmol of silane, 3 mmol of the required 1-alkyne, 3 mL of toluene and 0,1 mol % of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 mm Hg), by a steel siphon. The reactor was pressurized with carbon monoxide and the mixture was stirred at room temperature for 24 h, unless otherwise specified. After removal of excess CO (fume hood), the reaction

mixture was diluted with n-hexane, filtered on Celite and concentrated under vacuum. The residue was purified by column chromatography on silica gel with the appropriate solvent mixture as eluent.

General procedure for the fluoride promoted migration reaction. In a typical run, 2 mmol of the substrate, dissolved in 10 mL of anhydrous THF, were added slowly, at room temperature, to 5 mL of TBAF (1 M in THF). Immediately after the addition, the reaction mixture was hydrolyzed with water and extracted 3 times with ether, then the organic layers dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel, with the appropriate solvent mixture as eluent.

(*R*)(*S*)-2-[(1-Naphthyl)methyl]hexanal, 4ab. Isolated yield (*n*Hexane/Ethyl ether 95/5): 0.25 g, 52%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.23-1.78 (m, 6 H), 2.72-2.87 (m, 1 H), 3.11 (dd, *J* = 7.0, 14.4 Hz, 1 H), 3.46 (dd, *J* = 7.3, 14.4 Hz, 1 H), 7.29-7.56 (m, 4 H), 7.71-8.00 (m, 3 H), 9.70 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$) δ= 13.8, 22.7, 29.0, 29.1, 32.3, 52.3, 123.3, 125.3, 125.6, 126.1, 127.1, 127.3, 128.9, 131.7, 134.0, 134.9, 204.5 ppm. GC-MS, m/z (int. rel. %): 280 (M^+, 15), 165 (15), 141 (100), 128 (15); 115 (22); 41 (19). IR (neat) *v*: 2725 (CHO), 1722 (C=O) cm^{-1}. $C_{17}H_{20}O$ (240.15): calcd C, 84.96; H, 8.39; found: C, 84.88; H, 8.40.

(*R*)(*S*)-2-[(2-Naphthyl)methyl]hexanal, 4ac. Isolated yield (*n*Hexane/Ethyl ether 90/10) 0.24 g, 50%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.0 Hz, 3 H), 1.19-1.62 (m, 6 H), 2.56-2.71 (m, 1 H), 2.83 (dd, *J* = 7.0, 13.9 Hz, 1 H), 3.11 (dd, *J* = 7.3, 13.9 Hz, 1 H), 7.24 (dd, *J* = 8.7, 1.6 Hz, 1 H), 7.34-7.45 (m, 2 H), 7.55 (t, *J* = 1.6 Hz, 1 H), 7.70-7.77 (m, 3 H), 9.63 (d, *J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.7, 22.6, 28.2, 29.0, 35.0, 53.1, 125.3, 125.9, 127.1, 127.2, 127.3, 127.5; 128.0; 132.1, 133.4, 136.4, 204.4 ppm. GC-MS, (int. rel. %): 240 (M^+, 16), 165 (10), 155 (11), 141 (100), 128 (16), 115 (28), 41 (26); IR, *v*: 2722(CHO), 1722(C=O) cm^{-1}. $C_{17}H_{20}O$ (240.15): calcd C, 84.96, H, 8.39; found: C, 85.00; H, 8.37.

(*R*)(*S*)-2-(4-Fluorobenzyl)hexanal, 4ad. Isolated yield (*n*Hexane/Ethyl ether 80/20) 0.30 g, 73%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 5.9 Hz, 3 H), 1.19-1.65 (m, 6 H), 2.48-2.66 (m, 1 H), 2.67 (dd,

J = 6.6, 13.8 Hz, 1 H), 2.94 (dd, *J* = 7.1, 13.8 Hz, 1 H), 6.90-6.99 (m, 2 H), 7.06-7.14 (m, 2 H), 9.63 (d, *J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.7, 22.6, 28.1, 28.9, 34.0, 53.4, 115.1 (d, *J* = 20.9 Hz), 130.2 (d *J* = 7.6 Hz), 134.5 (d, *J* = 3.4 Hz), 161.4 (d, *J* = 244.2 Hz), 204.2 ppm. GC-MS, m/z (int. rel. %): 208 (M^+, 7), 166 (19), 151 (45), 109 (100), 83 (12), 41 (7). IR (neat) *v*: 2714 (CHO), 1724 (C=O) cm^{-1}. $C_{13}H_{17}FO$ (208.13): calcd C, 74.97, H, 8.23, F, 9.12.; found: C, 75.15, H, 8.20, F, 9.09.

(*R*)(*S*)-2-(4-(Dimethylamino)benzyl)hexanal, 4ae. Isolated yield (*n*Hexane/Ethyl ether 90/10): 0.32 g, 70%. ^{1}H NMR (200 MHz, $CDCl_3$): δ =0.88 (*J* = 6.2 Hz, 3 H), 1.22-1.72 (m, 6 H), 2.47-2.60 (m, 1 H), 2.63 (dd, *J* = 7.0, 20.2 Hz, 1 H), 2.90 (dd, *J* = 7.0, 20.2 Hz, 1 H), 2.91 (s, 6 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 9.64 (*J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.7, 22.6, 28.2, 29.1, 35.0, 40.6, 53.6, 112.7, 126.5, 129.5, 149.2, 205.1 ppm. GC-MS, m/z (int. rel. %): 233 (M^+, 7), 134 (100), 118 (8), 91 (5), 41 (12). IR (neat) *v*: 2704(CHO), 1720 (C=O) cm^{-1}. $C_{15}H_{23}NO$ (233.18): calcd C, 77.21, H, 9.93, N, 6.00; found: C, 77.35, H, 9.90, N, 5.98.

(*R*)(*S*)-2-Benzyloct-7-ynal, 4ba. Isolated yield (*n*Hexane/Ethyl ether 80/20): 0.33 g, 78%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26-1.57 (m, 6 H), 1.83 (t, *J* = 2.5 Hz, 1 H), 2.01-2.09 (m, 2 H), 2.47-2.60 (m, 1 H), 2.61 (dd, *J* = 7.0, 13.5 Hz, 1 H), 2.88 (dd, *J* = 6.9, 13.5 Hz, 1 H), 7.03-7.18 (m, 5 H), 9.55 (d, *J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 18.0, 25.8, 27.8, 28.2, 34.8, 53.1, 68.4, 83.9, 126.2, 128.4, 128.8, 138.6, 204.2 ppm. GC-MS, m/z (int. rel. %): 214 (M^+), 133 (26), 105 (12), 91 (100), 65 (14). IR (neat) *v*: 3293 (≡C-H), 2713 (CHO), 1723 (C=O) cm^{-1}. $C_{15}H_{18}O$ (214.14): calcd C, 84.07, H, 8.47; found: C, 84.24, H, 8.50.

(*R*)(*S*)- 2-Benzylhept-6-enal, 4ca. Isolated yield (*n*Hexane/Ethyl ether 90/10): 0.27 g, 67%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.23-1.68 (m, 4 H), 1.94 (m, 2 H); 2.45-2.60 (m, 1 H), 2.62 (dd, *J* = 6.8, 13.4 Hz, 1 H), 2.90 (dd, *J* = 7.3, 13.4 Hz, 1 H), 4.82-4.95 (m, 2 H), 5.66 (ddt *J* = 6.6, 10.3, 16.9 Hz, 1 H), 7.04-7.23 (m, 5 H), 9.56 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.1, 27.9, 33.5, 34.9, 53.2, 114.8, 126.3, 128.4, 128.9, 137.9, 138.8, 204.3 ppm. GC-MS, m/z (int. rel. %): 202 (M^+, 3), 133

(16), 117 (11), 91 (100), 78 (8), 65 (12), 41 (15). IR (neat) *v*: 3062 (=C-H), 2708 (CHO), 1723 (C=O); 1638(C=C) cm^{-1}. $C_{14}H_{18}O$ (202.14): calcd. C, 83.12, H, 8.97; found: C, 82.91, H, 8.93.

(*R*)(*S*)-2-Benzyl-6-cyanopentanal, 4da. Isolated yield (*n*Hexane/Ethyl acetate 50/50): 0.23 g, 58%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.50-1.88 (m, 4 H), 2.32 (t, *J* = 6.7 Hz, 2 H), 2.59-2.74 (m, 1 H), 2.73 (dd, *J* = 7.2, 13.4 Hz, 1 H), 3.05 (dd, *J* = 6.4, 13.4 Hz, 1 H), 7.16-7.33 (m, 5 H), 9.69 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.0, 22.7, 27.1, 34.9, 2.4, 119.0, 126.5, 128.5, 128.7, 137.8, 203.3 ppm. GC-MS, m/z (int. rel. %): 183 (M^+-18, 4), 172 (39), 144 (21), 133 (32), 105 (13), 91 (100), 65 (13), 51 (19), 41 (31). IR, *v*: 2716 (CHO), 2247 (C≡N), 1722 (C=O) cm^{-1}. $C_{13}H_{15}NO$ (201.11): calcd. C, 77.58, H, 7.51, N, 6.96; found C, 77.72, H, 7.48, N, 6.99.

(*R*)(*S*)-2-Benzyl-6-hydroxyhexanal, 4ea. Isolated yield (dichloromethane/acetone 80/20): 0.22 g, 53%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26–1.74 (m, 6 H), 2.54–2.70 (m, 1 H), 2.73 (dd, *J* = 6.8, 13.0 Hz, 1 H), 2.99 (dd, *J* = 7.2, 13.0 Hz, 1 H), 3.22 (s, 1 H), 3.56 (t, *J* = 6.1 Hz, 2 H), 7.14-7.33 (m, 5 H), 9.64 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 22.9, 28.0, 32.2, 34.7, 53.1, 61.8, 126.1, 128.2, 128.6, 138.5, 204.6 ppm. GC-MS, m/z (int. rel. %): 206 (M^+, 3), 188 (35), 170 (8), 144 (13), 133 (20), 117 (23), 104 (15), 91 (100), 77 (12), 65 (27), 39 (18). IR (neat) *v:* 3384 (O-H), 2720 (CHO), 1721 (C=O) cm^{-1}. $C_{13}H_{18}O_2$ (206.13): calcd. C, 75.69, H, 8.80; found: C, 75.78, H, 8.77.

(*R*)(*S*)-2-Benzyl-5-chloropentanal, 9. Isolated yield (*n*Hexane/Ethyl ether 90/10): 0.10 g, 25% ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.58–1.87 (m, 4 H), 2.57–2.71 (m, 1 H), 2.72 (dd, *J* = 6.7, 14.0 Hz, 1 H), 3.01 (dd, *J* = 7.0, 14.0 Hz, 1 H), 3.48 (t, *J* = 6.0 Hz, 2 H), 7.14-7.33 (m, 5 H), 9.65 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 25.5, 29.6, 34.9, 44.4, 52.4, 126.4, 128.4, 128.7, 138.2, 203.7 ppm. IR (neat) *v*: 2719 (CHO), 1724 (C=O) cm^{-1}. $C_{12}H_{15}ClO$ (210.08): calcd. C, 68.40, H, 7.18, Cl, 16.83; found: C, 68.63, H, 7.20, Cl, 16.78.

(*R*)(*S*)-2-Benzyl-6-chlorohexanal, 12. Isolated yield (*n*Hexane/Ethyl ether 90/10): 0.06 g, 13.5%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.42–1.77 (m, 6 H), 2.54–2.70 (m, 1 H), 2.72 (dd, *J* = 6.8, 14.0 Hz, 1 H), 3.00 (dd, *J* = 6.8, 14.0 Hz, 1 H), 3.48 (t, *J* = 6.6 Hz, 2 H), 7.13-7.30 (m, 5 H), 9.66 (d, *J* = 2.2 Hz, 1 H)

ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.1, 27.6, 32.3, 34.9, 44.5, 53.1, 126.4, 128.5, 128.8, 138.5, 204.1 ppm. IR (neat) *v*: 2720 (CHO), 1724 (C=O) cm^{-1}. $C_{13}H_{17}ClO$ (224.09): calcd. C, 69.48, H, 7.62, Cl, 15.78; found: C, 69.29, H, 7.60, Cl, 15.83.

1-Benzyl-2-isobutylcyclopentanecarbaldehyde (diastereomeric mixture, *Z/E* = 70/30), 13. Isolated yield (*n*Hexane/Ethyl ether 90/10): 0.24 g, 49%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 6.2 Hz, 6 H), 1.05 (d, *J* = 6.2 Hz, 6 H), 1.32-2.09 (m, 20 H), 2.44 (d, *J* = 13.9 Hz, 0.6 H), 2.85 (d, *J* = 13.7 Hz, 1.4 H), 3.28 (d, *J* = 13.7 Hz, 1.4 H), 3.39 (d, *J* = 13.9 Hz, 0.6 H), 7.21-7.37 (m, 10 H), 9.51 (s, 0.6 H), 9.87 (s, 1.4 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$), δ 20.9 and 21.5, 22.2 and 22.3, 24.1 and 23.8, 26.8 and 26.3, 30.8 and 29.8, 31.0 and 31.1, 37.9 and 32.8, 39.0 and 39.2, 46.8 and 43.1, 59.9 and 60.9, 126.1 and 125.9, 127.9, 130.0 and 130.1, 137.7 and 138.6, 206.4 and 205.0 ppm. GC-MS, m/z (int. rel. %)(minor diastereomer): 245 (M^++1, 62), 227 (22), 188 (100), 171 (12), 158 (15), 120 (17); GC-MS, m/z (int. rel. %)(major diastereomer) 245 (M^++1, 75); 188 (100); 171 (25); 120 (22). IR (neat) *v*: 2710 (CHO), 1691 (C=O) cm^{-1}.

1-Benzyl-2-methylcyclohexanecarbaldehyde (diastereomeric mixture, *Z/E* = 70/30), 14. Isolated yield (*n*Hexane/Ethyl ether 90/10): 0.18 g, 41%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 7.0 Hz, 4.2 H), 1.17 (d, *J* = 7.0 Hz, 1.8 H), 1.26-2.02 (m, 18 H), 2.65 (d, *J* = 13.8 Hz, 1.4 H), 2.78 (d, *J* = 13.7 Hz, 0.6 H), 3.03 (d, *J* = 13.7 Hz, 0.6 H), 3.08 (d, *J* = 13.8 Hz, 1.4 H), 7.15-7.35 (m, 10 H), 9.56 (s, 1.4 H), 9.92 (s, 0.6 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.4 and 16.3, 21.1 and 22.3, 23.6 and 24.7, 27.5 and 29.7, 30.1 and 31.4, 33.3 and 34.7, 36.7 and 40.3, 53.4 and 52.4, 126.1 and 126.4, 128.0, 130.3 and 130.4, 137.4 and 136.7, 207.2 and 207.4 ppm. IR (neat) *v*: 2699 (CHO), 1721 (C=O) cm^{-1}.

2-Benzyl-3-methylpent-2-enal (diastereomeric mixture, *Z/E* = 57/43), 17. Isolated yield (*n*Hexane/Ethyl ether 80/20): 0.23 g, 62%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.8 Hz, 2.58 H), 1.26 (t, *J* = 7.6 Hz, 3.42 H), 2.07 (s, 3.42 H), 2.31 (s, 2.58 H), 2.41 (q, *J* = 7.8 Hz, 1.72 H), 2.74 (q, *J* = 7.6 Hz, 2.28 H), 3.73 (s, 2.28 H), 3.75 (s, 1.72 H), 7.19-7.35 (m, 10 H); 10.28 (s, 1.14 H), 10.31 (s, 0.86 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.2 and 11.6, 21.5 and 16.7, 26.2 and 30.1, 30.7 and 30.7,

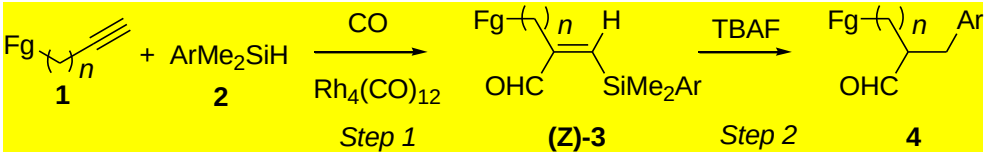
125.7 (2C), 128.0 (2C), 128.2 (2C), 135.3 and 135.0, 139.9 and 140.3, 162.6 and 161.5, 190.2 and 191.3 ppm. GC-MS, m/z (int. rel. %) (major diastereomer): 188 (M^+, 48), 159 (74), 141 (13), 131 (42), 129 (26), 117 (26), 115 (31), 105 (17), 91 (89), 77 (19), 65 (27), 53 (25), 51 (44), 46 (45), 41 (40), 39 (100); GC-MS, m/z (int. rel. %) (minor diastereomer): 188 (M^+, 43), 173 (5), 159 (77), 141 (13), 131 (42), 129 (28), 115 (33), 105 (18), 91 (91), 77 (19), 65 (27), 51 (44), 43 (44), 41 (88), 39 (100). IR (neat) *v*: 3021 (C=C-H), 2756 (CHO), 1660 (C=O), 1616 (C=C) cm^{-1}.

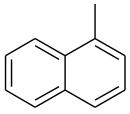
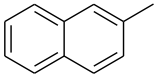
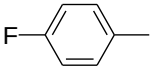
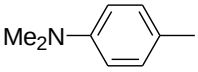
2-Benzyl-3-methyl-3-(tert-butoxycarbonylamino)-pentanal, 18. Isolated yield (CH_2Cl_2): 0.33 g, 54%. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.4 Hz, 3 H), 1.00 (t, *J* = 7.4 Hz, 3 H), 1.27 (s, 3 H), 1.40 (s, 3 H), 1.53 (m, 11 H), 1.55 (m, 11 H), 2.83 (t, *J* = 12.6 Hz, 1 H), 2.85 (t, *J* = 12.6 Hz, 1 H), 3.12 (t, *J* = 12.6 Hz, 1 H), 3.14 (t, *J* = 12.6 Hz, 1 H), 3.73 (m, 1 H), 3.76 (m, 1 H), 4.74 (s, 1 H), 4.84 (s, 1 H), 7.22-7.36 (m, 10 H), 9.84 (d, *J* = 2.4 Hz, 1 H), 9.87 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 7.6 and 7.3, 1.2 and 21.9, 28.3 and 29.5, 30.7 and 30.4, 51.1 and 53.3, 57.2 and 57.0, 60.3 and 59.6 79.2 (2C), 125.9 and 126.0, 128.3 (2C), 128.9 (2C), 139.8 and 139.7, 154.1 and 154.3, 203.9 and 204 ppm. GC-MS, m/z (int. rel. %): 134 (37), 116 (62), 92 (48), 91 (100), 72 (46), 57 (79), 42 (40), 41 (47), 39 (33). IR (neat) *v* 3021 (N-H), 2732 (CHO), 1713 (C=O) cm^{-1}. $C_{18}H_{27}NO_3$ (305.20): calcd. C, 70.79, H, 8.91, N, 4.59; found: 70.91; H, 8.93, N, 4.61.

(*E*)-2-Benzyl-4,4-dimethyl-pent-2-enal, 21. Isolated yield (CH_2Cl_2): 0.12 g, 31%. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.20 (s, 9 H), 3.80 (s, 2 H), 6.58 (s, 1 H), 7.10-7.35 (m, 5 H), 9.41 (s, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.4, 29.5, 30.1, 125.9, 127.9, 128.3, 139.2, 139.3, 166.0, 196.4 ppm.; GC-MS, m/z (int. rel. %): 202 (M^+, 36), 159 (40), 145 (32), 131 (53), 115 (37), 91 (85), 77 (8), 55 (23), 43 (40), 41 (100), 39 (89). IR (neat) *v*: 3025 (C=C-H), 2708 (CHO), 1685 (C=O), 1632 (C=C). $C_{14}H_{18}O$ (202.29): calcd C, 83.12; H, 8.97; found: C, 83.38, H, 8.92.

Supporting infarmation (See footnote on the first page of this article)**:** Procedures and spectral data for the silylformylation products **(*Z*)-3ab-(*Z*)-3ea**, **(*Z*)-6c-(*Z*)-20**.

Table 1. Silylformylation-Aryl Migration Reactions of Terminal Acetylenes and Aryldimethylsilanes

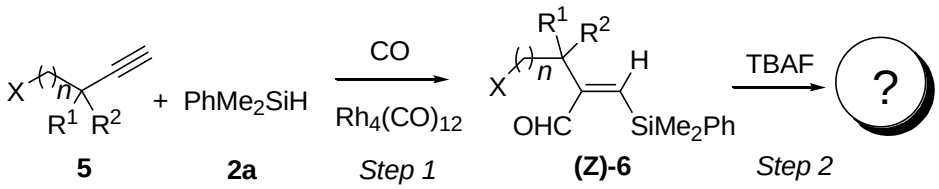


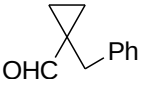
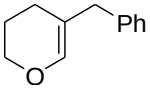
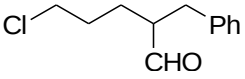
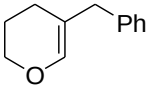
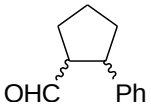
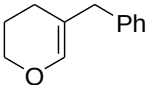
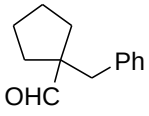
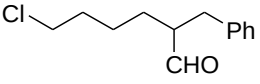
Entry	**1**	Fg	*n*	**2**	Ar	P_{CO} (atm)	***(Z)*-3**	Yield (%)[c]	**4**	Yield (%)[c]
					step 1: silylformylation[a]				*step 2: aryl migration*[b]	
1	**a**	H	4	**b**		30	**ab**	99 (74)	**ab**	100 (52)
2	**a**	H	4	**c**		30	**ac**	98 (81)	**ac**	100 (50)
3	**a**	H	4	**d**		30	**ad**	94 (66.5)[d]	**ad**	100 (73)
4	**a**	H	4	**e**		30	**ae**	98 (63)	**ae**	100 (70)
5	**b**	C≡CH	4	**a**	Ph	40	**ba**	70 (28)[e]	**ba**	100 (78)
6	**c**	HC=CH$_2$	3	**a**	Ph	10	**ca**	100 (82)	**ca**	100 (67)
7	**d**	CN	3	**a**	Ph	10	**da**	99 (87)	**da**	100 (58)
8	**e**	OH	4	**a**	Ph	20	**ea**	74 (55)[f]	**ea**[g]	100 (53)

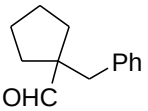
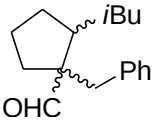
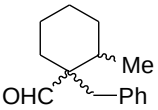
[a] Reaction conditions: 3 mmol of alkyne **1**, 3 mmol of silane **2**, 3 mL of toluene, 0.1 mmol % of $Rh_4(CO)_{12}$, room temperature, 24 hs. [b] Reaction conditions: 2 mmol of aldehydes ***(Z)*-3** added to 5mL of TBAF (1M in THF) in 10 mL of THF and immediately hydrolysed. [c] Determined by GC analysis; in parentheses the isolated yields are reported (not optimised). [d] Reaction time: 41hs. [e]Reaction performed with alkyne:silane ratio = 2:1, 0.2 mol % of catalyst; 30% of doubled silylated by-products. [f]

Diastereomers mixture: *Z/E* = 60/40; 26% of phenyldimethylsilyloxy aldehydes. [g] The mixture of *Z/E* diastereomers yielded **4ea** as sole product.[7a]

Table 2. Silylformylation-Phenyl Migration Reactions of Acetylenes Characterised by the Presence of a Leaving Group



Entry	5	X	R^1, R^2	*n*	P_{CO} (atm)	(Z)-6	Yield (%)[c]	Products, yield (%)[c]
					Step 1: silylformylation[a]			*Step 2: phenyl migration*[b]
1[7b]	**a**	Br	H, H	1	35	**a**	100 (62)	 **7**, 100 (90)[7b]
2	**b**	Cl	H, H	2	20	**b**	99 (69)	 **8**, 60 (52)[10]  **9**, 40 (25)
3	**c**	Br	H, H	2	30	**c**	100 (82)	 **8**, 75 (43)[10]  **10**, 25 (9.5, *E*/*Z* =90/10)[11]
4	**d**	OTs	H, H	2	40	**d**	95	 **8**, 100 (75)[10]
5	**e**	Cl	H, H	3	30	**e**	99 (77)	 **11**, 73 (58)[7b]  **12**, 27 (13.5)

6[7b]	**f**	Br	H, H	3	10	**f**	100 (87)	 **11**, 100 (82) [7b]
7	**g**	I	H, *i*Bu	3	50	**g**	99 (55)	 **13**, 100 (49, *Z/E*=70/30)
8	**h**	Br	H, Me	4	40	**h**	99 (60)	 **14**, 100 (41, *Z/E*=70/30)

[a] Reaction conditions: 3 mmol of alkyne **1**, 3 mmol of silane **2**, 3 mL of toluene, 0.1 mmol % of $Rh_4(CO)_{12}$, room temperature, 24 hs. [b] Reaction conditions: 2 mmol of aldehydes **(*Z*)-3** added to 5 mL of TBAF (1M in THF) in 10 mL of THF and immediately hydrolysed. [c] Determined by GC analysis; in parentheses the isolated yields are reported (not optimised). [d] Crude product (diastereomers mixture: *Z/E*=80/20)

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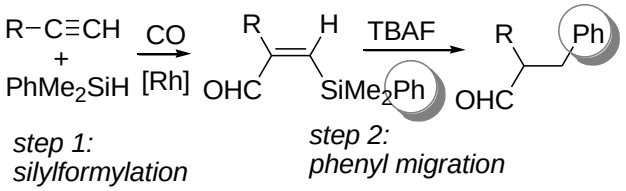
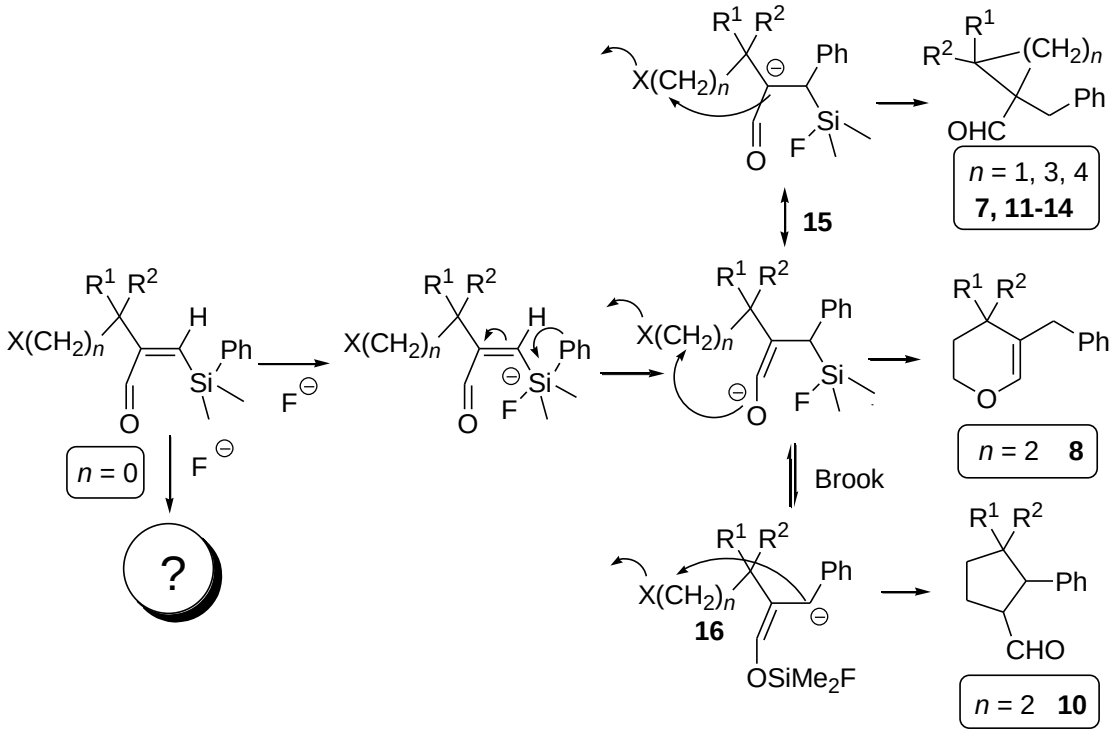
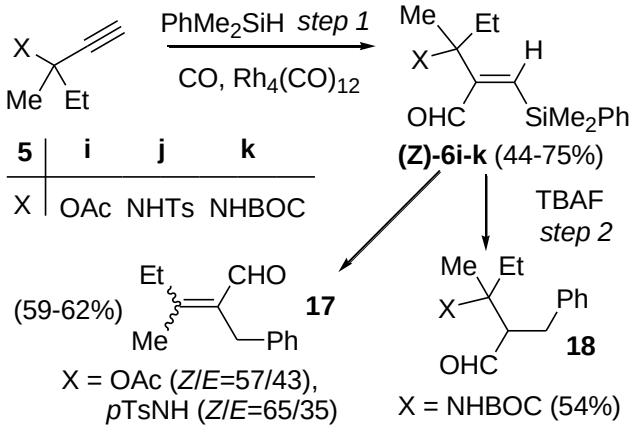

R−C≡CH
+
PhMe2SiH
CO
[Rh]
R
H
OHC
SiMe2Ph
TBAF
R
Ph
OHC
step 1:
silylformylation
step 2:
phenyl migration

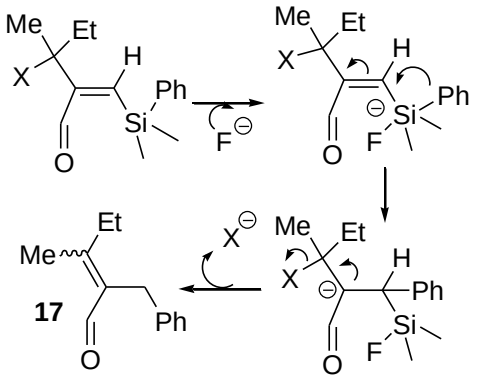
Scheme 1


R1 R2
X(CH2)n
Ph
Si
F
O
R1
R2
(CH2)n
Ph
OHC
n = 1, 3, 4
7, 11-14
15
H
n = 0
F
?
Brook
n = 2 8
CHO
16
OSiMe2F
n = 2 10

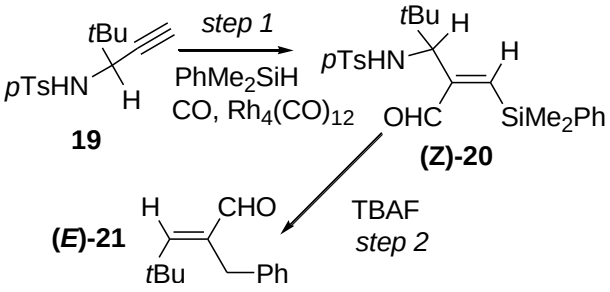
Scheme 2


X
Me Et
PhMe2SiH step 1
CO, Rh4(CO)12
Me Et
X H
OHC SiMe2Ph
(Z)-6i-k (44-75%)
5 i j k
X OAc NHTs NHBOC
TBAF
step 2
Et CHO
(59-62%)
17
Me Ph
X = OAc (Z/E=57/43),
pTsNH (Z/E=65/35)
Me Et
X Ph
OHC
18
X = NHBOC (54%)

Scheme 3



Scheme 4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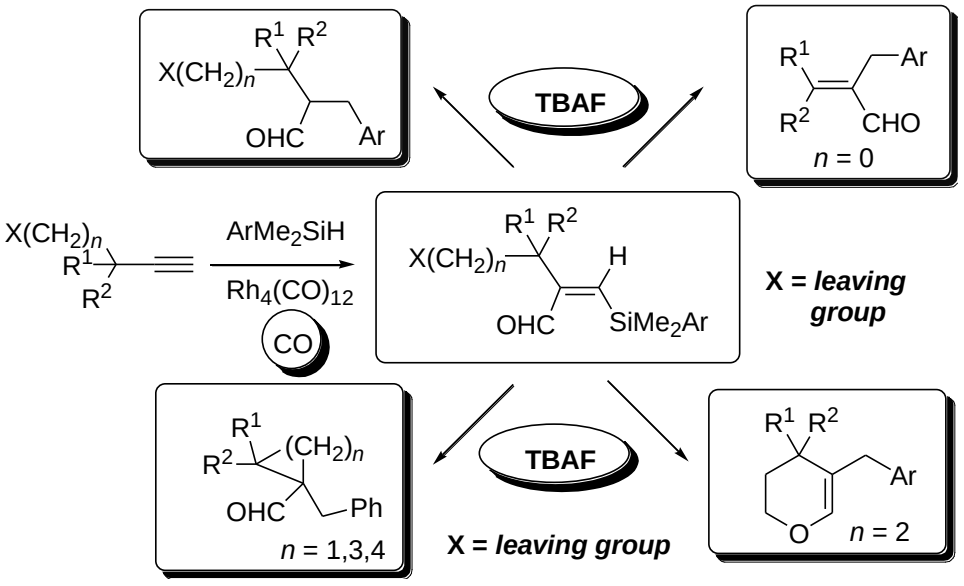
pTsHN
H
19
step 1
PhMe2SiH
CO, Rh4(CO)12
tBu
H
pTsHN
H
OHC
SiMe2Ph
(Z)-20
TBAF
step 2
H
CHO
(E)-21
tBu
Ph

Scheme 5

Graphical Abstract



Tandem Silylformylation and Fluoride-Assisted Aryl Migration: a Versatile Approach to the Synthesis of Polyfunctionalised Compounds

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Eur. J. Org. Chem.

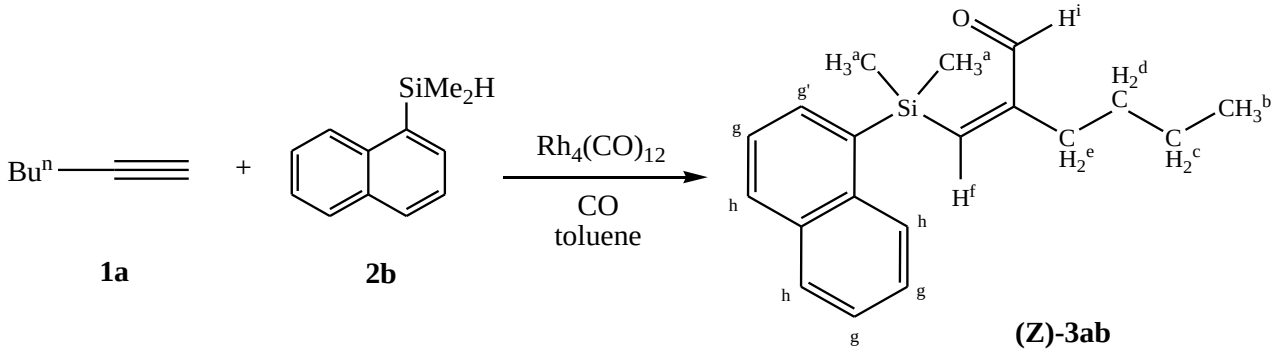
Supporting Information

Contents:

General remarks. All solvents were reagent grade materials purified by standard methods. THF and toluene were distilled from sodium immediately before use. All silanes **2** were distilled and stored under inert gas. Non commecial silanes **2b-e** were prepared from the corrisponding Grignard reagents according to the method described by Hiyama and co-workers.[1] Commercial 1-alkynes were distilled before use. $Rh_4(CO)_{12}$ was prepared and purified as previously reported.[2] **5d** and **5g-h** were prepared according to literature methods.[3] ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded in $CDCl_3$ solution with Me_4Si or $CHCl_3$ as internal standards; δ value are given in ppm and coupling constants (*J*) in Hz. The *Z/E* configurations were determined by means of NOE experiments. Infrared absorption spectra were recorded as neat films. Mass spectra were obtained with a Perkin-Elmer Q-Mass 910 connected to a Perkin-Elmer 8500 gas chromatograph. GLC analyses were performed with a DB1 capillary column (30 m x 0.52 mm, 5 micron) using He as the carrier gas and a flame ionisation detector (FID). Column chromatography was performed on silica gel 60 (230-400 mesh). All products were identified and characterised by spctroscopic and analitical data. Spectra for **(*Z*)-3da**[4], **(*Z*)-6a**[5], **(*Z*)-6b**[6], **(*Z*)-6f**[5] perfectly agreed with literature.

General procedure for the Rhodium-catalyzed silylformylation. Carbonylation reactions were run in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 3 mmol of silane, 3 mmol of the required 1-alkyne, 3 mL of toluene and 0,1 mol % of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, previously placed under vacuum (0,1 mm Hg), by a steel siphon. The reactor was pressurized with carbon monoxide and the mixture was stirred at room temperature for 24 h, unless otherwise specified. After removal of excess CO (fume hood), the reaction mixture was diluted with n-hexane, filtered on Celite and concentrated under vacuum. The residue was purified by column chromatography on silica gel with the appropriate solvent mixture as eluent.

Preparation of (*Z*)-2-[(dimethyl(1-naphtyl)silyl)methylene]hexanal, (*Z*)-3ab.



Following the general silylformylation procedure, 0.559 g (3 mmol) of 1-naphtyldimethylsilane, **2b**, 0,34 mL of 1-hexyne, **1a**, (3 mmol, d = 0.71 g/mL), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, by a steel siphon and the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 95/5, affording 0.67 g of **(*Z*)-3ab** as a colorless oil (74 % yield).

^{1}H-NMR, δ: 0.66 (6H, H_a, s); 0.89 (3H, H_b, t, J_{bc} = 7.0 Hz); 1.22–1.50 (4H, H_c + H_d, m); 2.30 (2H, H_e, t, J_{ed} = 7.0 Hz); 7.14 (1H, H_f, s); 7.43-7.50 (3H, H_g, m); 7.74 (1H, $H_{g'}$, dd, J = 1.2 Hz, 7.0 Hz); 7.85-7.92 (3H, H_h, m); 9.73 (1H, H_i, s).

^{13}C-NMR, δ: 0.7; 13.8; 22.3; 30.5; 31.5; 125.2; 125.6; 125.9; 128.1; 129.3; 130.5; 133.4; 133.6; 136.0; 136.1; 149.8; 156.9; 193.2.

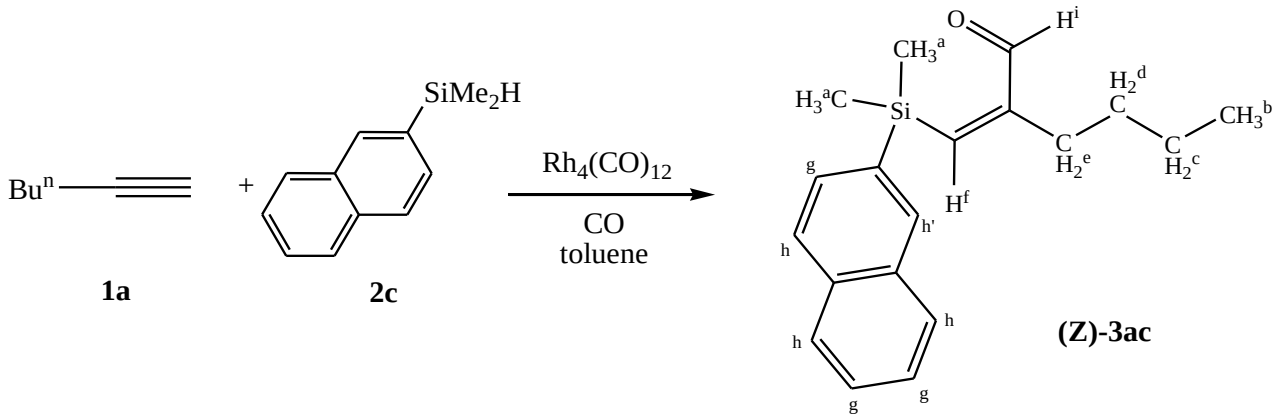
GC-MS, m/z (int. rel. %): 296 (M^+, 2); 281 (36); 251 (18); 239 (21); 221 (21); 195 (100); 179 (36); 169 (42); 155 (22); 127 (58); 75 (31); 59 (21); 53 (20).

IR, ν 2735; 1682; 1583; 1252.

Analysis: $C_{19}H_{24}OSi$ (296.16)

Calculated	C, 76.97;	H, 8.16%
Found	C, 76.76;	H, 8.19%

Preparation of (*Z*)-2-[(dimethyl(2-naphtyl)silyl)methylene]hexanal, (*Z*)-3ac



Following the general silylformylation procedure, 0.559 g (3 mmol) of 2-naphtyldimethylsilane, **2c**, 0,34 mL of 1-hexyne, **1a**, (3 mmol, d = 0.71 g/mL), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 95/5, affording 0.77 g of **(*Z*)-3ac** as a colorless oil (81 % yield).

^{1}H-NMR, δ: 0.57 (6H, H_a s); 0.90 (3H, H_b, t, J_{bc} = 7.0 Hz); 1.22-1.46 (4H, H_c + H_d, m); 2.31 (2H, H_e, t, J_{ed} = 7.0 Hz); 6.97 (1H, H_f, s); 7.46-7.50 (3H, H_g, m); 7.79-7.84 (3H, H_h, m); 7.99 (1H, $H_{h'}$, m); 9.79 (1H, H_i, s).

^{13}C-NMR, δ: -0.1; 13.9; 22.4; 30.6; 31.6; 126.2; 126.7; 127.5; 127.7; 128.1; 129.5; 132.9; 133.8; 134.3; 135.4; 148.8; 157.3; 193.2.

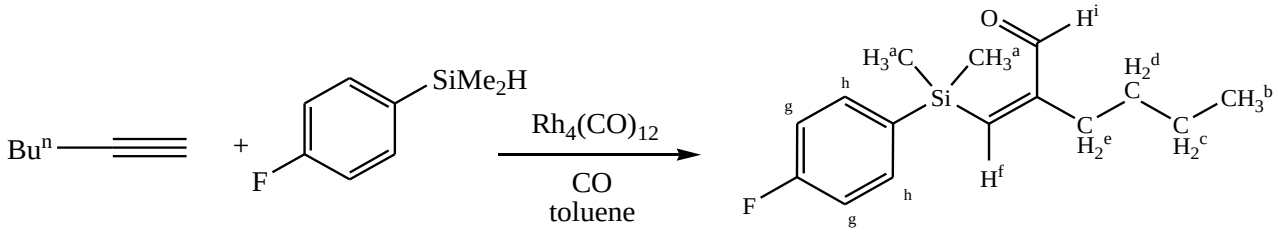
GC-MS, m/z (int. rel.. %): 296 (M^+, 2); 281 (50); 239 (81); 221 (27); 187 (28); 185 (43); 179 (60) ; 178 (23);171 (26); 169 (66); 167 (30); 165 (23); 155 (30); 141 (22); 128 (23);127 (85); 75 (30); 61 (26); 59 (20); 53 (26); 45 (21); 43 (100); 41 (61); 39 (39).

IR, ν: 2722; 1683; 1568; 1250.

Analysis: $C_{19}H_{24}OSi$ (296.16)

Calculated	C, 76.97;	H, 8.16%
Found	C, 77.15;	H, 8.18%

Preparation of (*Z*)-2-{[(4-fluorophenyl)dimethylsilyl]methylene}hexanal, (*Z*)-3ad



1a **2d** **(Z)-3ad**

Following the general silylformylation procedure, 0.462 g (3 mmol) of 4-Fluorophenyldymethylsilane, **2d**, 0,34 mL of 1-hexyne, **1a**, (3 mmol, d = 0.71 g/mL), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at room temperature for 41 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 95/5, affording 0.70 g of **(*Z*)-3ad** as a colorless oil (66.5 % yield).

^{1}H-NMR, δ: 0.49 (6H, H_a, s); 0.89 (3H, H_b, t, J_{bc} = 7.2 Hz); 1.22-1.48 (4H, H_c + H_d, m); 2.30 (2H, H_e, dt, J_{ed} = 7.0 Hz, J_{ef} = 0.8 Hz); 6.88 (1H, H_f, t, J_{fe} = 0.8 Hz); 7.05 (2H, H_g, m); 7.48 (2H, H_h, m); 9.75 (1H, H_i, s).

^{13}C-NMR, δ: -0.1; 13.8; 22.4; 30.6; 31.6; 115.3 (d, J^2_{CF} = 19.8 Hz); 133.6 (d, J^4_{CF} = 4.2 Hz); 135.4 (d, J^3_{CF} = 7.6 Hz); 148.2; 157.4; 163.8 (d, J_{1F} = 249 Hz); 192.9.

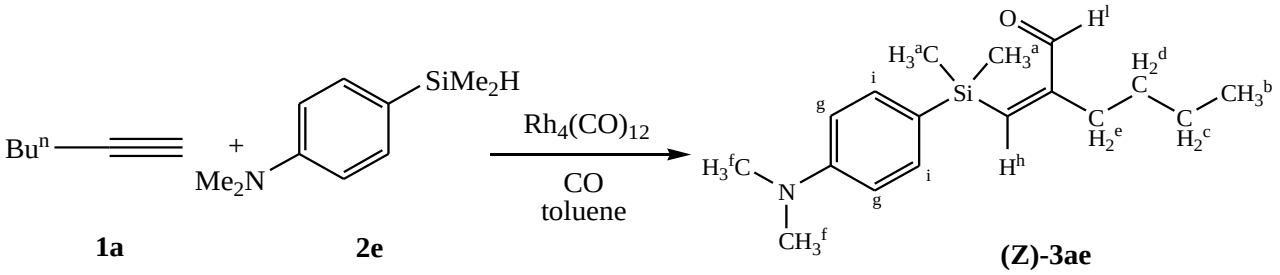
GC-MS, M/z (int. rel. %): 264 (M^+, 0.2); 249 (43); 208 (17); 207 (100); 169 (19); 155 (43); 153 (46); 147 (21); 140 (20); 139 (19); 127 (41); 98 (14); 91 (19); 75 (14); 47 (15).

IR, ν: 2731; 1682; 1585; 1500; 1247; 1158; 1103; 825.

Analysis: $C_{15}H_{21}FOSi$ (264.13)

Calculated	C, 68.14;	H, 8.01	F, 7.19%
Found	C, 68.30;	H, 8.03	F, 7.17%

Preparation of (*Z*)-2-{[(4-(dimethylamino)phenyl)dimethylsilyl]methylene}hexanal, (*Z*)-3ae



Following the general silylformylation procedure, 0.537 g (3 mmol) of 4-(Dimethylamino)phenyldimethylsilane, **2e**, 0,34 mL of 1-hexyne, **1a**, (3 mmol, d = 0.71 g/mL), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclaveby a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 90/10, affording 0.55 g of **(*Z*)-3ae** as a colorless oil (63 % Yield).

^{1}H-NMR, δ: 0.46 (6H, H_a, s); 0.91 (3H, H_b, t, J_{bc} = 7.0 Hz); 1.22-1.50 (4H, H_c + H_d, m); 2.29 (2H, H_e, t, J_{ed} = 7.2 Hz); 2.96 (6H, H_f, s); 6.72 (2H, H_g, d, J_{gi} = 8.8 Hz); 6.94 (1H, H_h, s); 7.38 (2H, H_i, d, J_{ig} = 8.8 Hz); 9.81 (1H, H_l, s).

^{13}C-NMR, δ: 0.1; 13.8; 22.4; 30.6; 31.4; 40.0; 112.0; 122.5; 134.6; 151.2; 150.5; 156.6; 193.7.

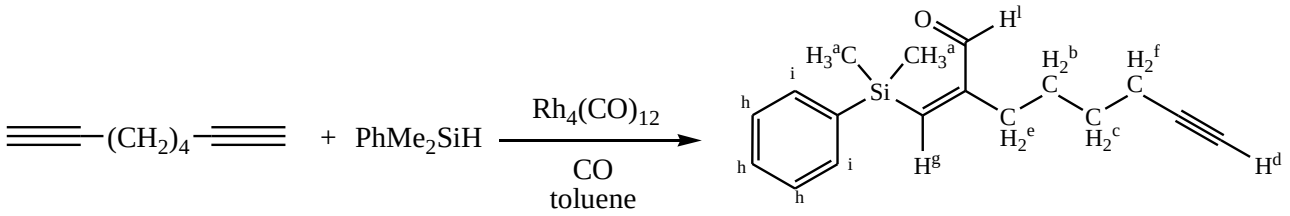
GC-MS, m/z (int. rel. %): 289 (M^+, 15); 274 (60); 232 (59); 214 (20); 180 (26); 178 (30); 172 (59); 164 (36); 162 (20); 134 (39); 121 (100); 120 (41); 98 (25); 59 (20); 43 (50); 42 (22); 41 (58); 39 (31).

IR, ν: 2740; 1683; 1597; 1515; 1353; 1243; 1110.

Analysis: $C_{17}H_{27}NOSi$ (289.18)

Calculated	C, 70.53;	H, 9.40;	N, 4.84%
Found	C, 70.70;	H, 9.44;	N, 4.80%

Preparation of (*Z*)-2-[(dimethyl(phenyl)silyl)methylene]oct-7-ynal, (*Z*)-3ba



1b **2a** **(Z)-3ba**

Following the general silylformylation procedure, 0.61 mL (4 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0,848 g of 1,7-octadiyne, **1b**, (8 mmol), 3 mL of toluene and 0,0060 g (0,2 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 40 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl acetate 95/5, affording 0.30 g of **(*Z*)-3ba** as a colorless oil (28 % Yield).

^{1}H-NMR, δ: 0.52 (6H, H_a, s); 1.52-1.60 (4H, H_b + H_c, m); 1.94 (1H, H_d, t, J_{df} = 2.8 Hz); 2.16-2.24 (2H, H_e, m); 2.29-2.36 (2H, H_f, m); 6.96 (1H, H_g, s); 7.35-7.38 (3H, H_h, m); 7.50-7.55 (2H, H_i, m); 9.78 (1H, H_l, s).

^{13}C-NMR, δ: -0.2; 18.1; 27.2; 27.9; 31.1; 68.3; 84.1; 128.0; 129.4; 133.4; 137.8; 149.0; 156.5; 192.9.

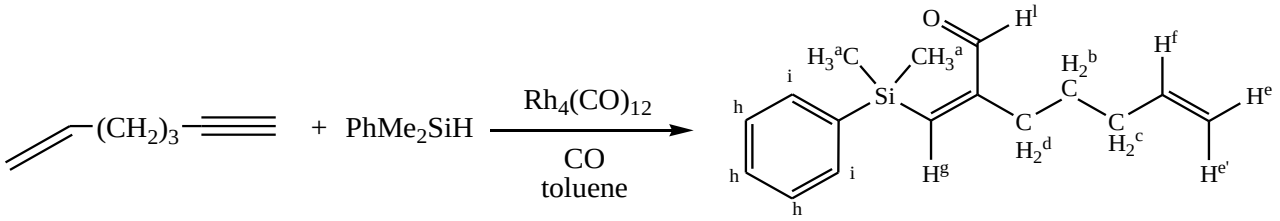
GC-MS, m/z (int. rel. %) : 255 (M^+-15, 2); 164 (15); 149 (18); 137 (100); 135 (40); 121 (28); 107 (15); 105 (30); 91 (34); 75 (51); 59 (15); 43 (17); 41 (17); 39 (19).

IR, ν: 3295; 2732; 2114; 1683; 1590; 1425; 1251; 1111.

Analysis: $C_{17}H_{22}OSi$ (270.14)

Calculated	C, 75.50;	H, 8.20%
Found	C, 75.38;	H, 8.22%

Preparation of (*Z*)-2-[(dimethyl(phenyl)silyl)methylene]hept-6-enal, (*Z*)-3ca



Following the general silylformylation procedure, 0.46 mL (3 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0,282 g of hept-1-en-6-yne, **1c**, (3 mmol), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, by a steel siphon, the reactor was pressurized with 10 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 95/5, affording 0.64 g of **(*Z*)-3ca** as a colorless oil (82 % yield).

^{1}H-NMR, δ: 0.51 (6H, H_a, s); 1.54 (2H, H_b, m); 2.07 (2H, H_c, q, $J_{cb} = J_{cf} = 6.6$ Hz); 2.33 (2H, H_d, t, $J_{db} = 7.5$ Hz); 4.92-5.01 (2H, $H_e + H_{e'}$, m); 5.80 (1H, H_f, ddt $J_{fc} = 6.6$ Hz, $J_{fe} = 10.3$ Hz, $J_{fe'} = 16.9$ Hz); 6.94 (1H, H_g, s); 7.35-7.38 (3H, H_h, m); 7.49-7.53 (2H, H_i, m); 9.77 (1H, H_l, s).

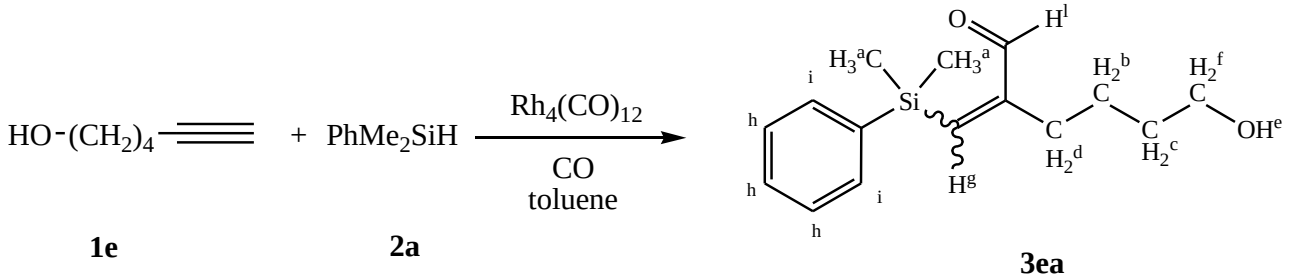
^{13}C-NMR, δ: -0.1; 27.6; 31.3; 33.3; 114.8; 128.1; 129.4; 133.5; 137.9; 138.3; 149.2; 156.8; 193.1.

GC-MS, m/z (int. rel. %): 257 (M^+ - 1); 137 (85); 135 (49); 105 (33); 75 (46); 43 (100); 39 (35).

Analysis: $C_{16}H_{22}OSi$ (258.14)

Calculated	C, 74.36;	H, 8.58%
Found	C, 74.52;	H, 8.60%

Preparation of 6-hydroxy-2-((dimethyl(phenyl)silyl)methylene)hexanal (diastereomeric mixture, *Z/E* = 60/40), 3ea



Following the general silylformylation procedure, 0.46 mL (3 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0,44 mL of 5-Hexyn-1-ol, **1e**, (3 mmol, d = 0.89 g/mL), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 20 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 90/10, affording 0.58 g of a diastereomeric mixture (*Z/E* = 60/40) of **3ea** as a yellow oil (55 % yield).

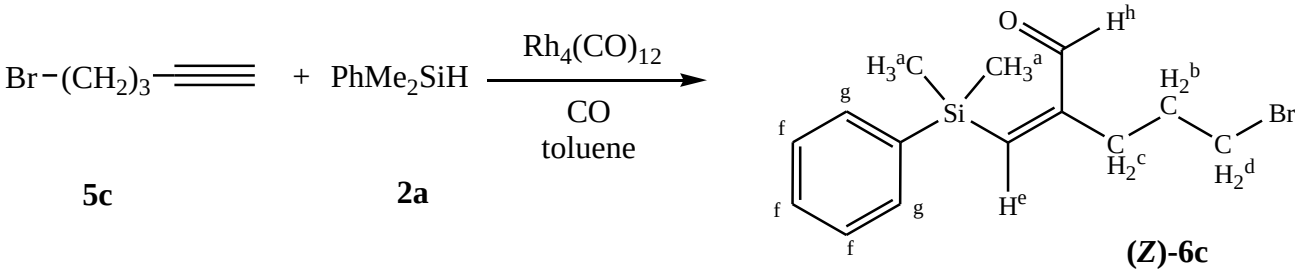
^{1}H-NMR, δ: 0.50 (12H, H_a, s); 1.16-1.63 (8H, H_b + H_c, m); 2.15-2.35 (4H, H_d, m); 2.6 (2H, H_e, br. s); 3.49 (1.6H, H_f, t, J_{fc} = 6.4 Hz); 3.59-3.65 (2.4 H, H_f, m); 6.79 (1.6H, H_g, s); 6.96 (2.4H, H_g, s); 7.32-7.39 (6H, H_h, m); 7.48-7.55 (4H, H_i, m); 9.39 (0.8H, H_l, s); 9.75 (1.2H, H_l, s).

^{13}C-NMR, δ: -1.9 and -0.2; 24.5 and 25.3; 27.9 and 31.4; 32.1 and 32.5; 62.0 and 62.2; 128.0 and 128.1; 129.4 and 129.5; 133.4 and 133.6; 136.9 and 137.8; 149.6 and 151.8; 157.5 and 156.6; 193.3 and 195.8.

GC-MS, m/z (int. rel. %) : 217 (M^+ - 45, 8); 156 (5); 137 (100); 135 (22); 121 (4); 105 (5); 91 (6); 75 (9); 61 (3).

IR, ν: 3336; 2940; 2709; 1678; 1425; 1249; 1105; 836; 732; 699.

Preparation of (*Z*)-5-bromo-2-[(dimethyl(phenyl)silyl)methylene]pentanal, (*Z*)-6c



Following the general silylformylation procedure, 0.61 mL (4 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.588 g of 5-Bromopentyne, **5c**, (4 mmol), 3 mL of toluene and 0,0030 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a

Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 90/10, affording 1.02 g of **(*Z*)-6c** as a pale yellow oil (82 % yield).

^{1}H-NMR, δ: 0.64 (6H, H_a, s); 2.06 – 2.14 (2H, H_b, m); 2.59 (2H, H_c, t, J_{cb} = 7.7 Hz); 3.46 (2H, H_d, t, J_{db} = 6.6 Hz); 7.15 (1H, H_e, s); 7.46 – 7.49 (3H, H_f, m); 7.63 – 7.66 (2H, H_g, m); 9.90 (1H, H_h, s).

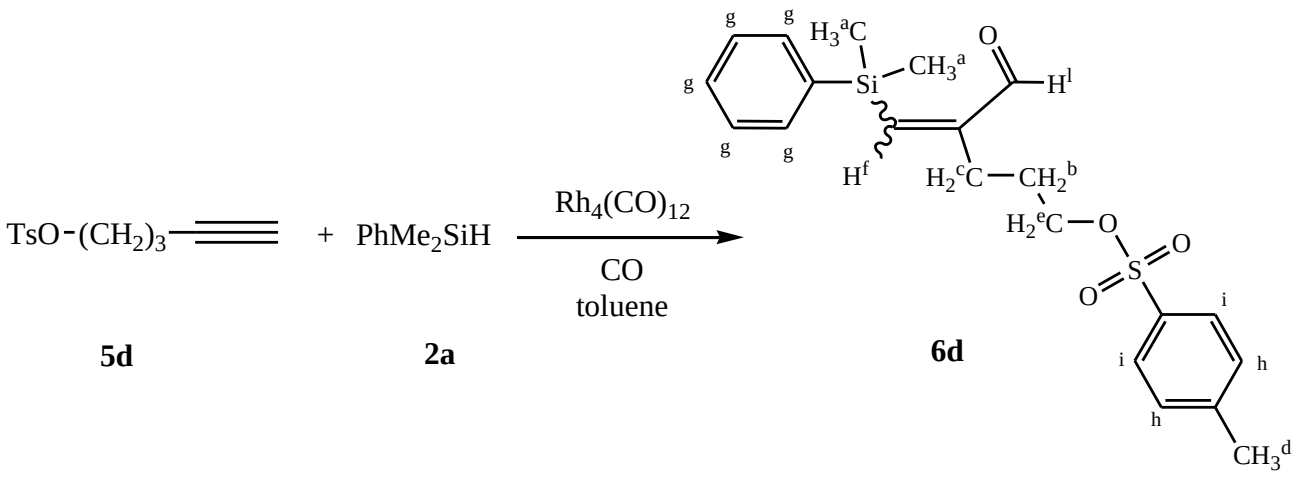
^{13}C-NMR, δ: -0.5; 30.5; 30.9; 32.6; 127.9; 129.2; 133.2; 137.3; 149.9; 154.6; 192.1.

IR, ν: 2738; 1684; 1590; 1428; 1250; 1113; 838; 733; 700.

Analysis: $C_{14}H_{19}BrOSi$ (310.04)

Calculated	C, 54.02;	H, 6.15;	Br, 25.67%
Found	C, 54.20;	H, 6.13;	Br, 25.57%

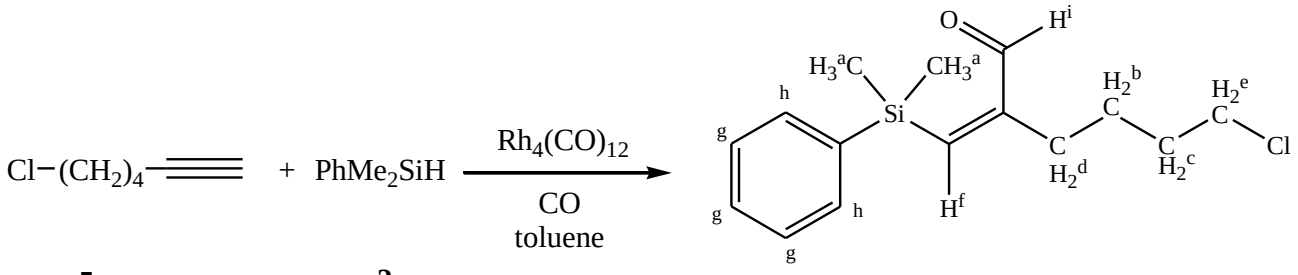
5-tosyloxy-2-[(dimethyl(phenyl)silyl)methylene]pentanal (diastereomeric misture, *Z/E* = 80/20), 6d



Following the general silylformylation procedure, 0.46 mL (3 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.714 g of 5-tosyloxypentyne, **5d**, (3 mmol), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, by a steel siphon, the reactor was pressurized with 40 atm of carbon monoxide and the mixture was stirred at room temperature for 40 h. After the usual work up the reaction afforded 1.14 g of crude **6d** (GC yield = 95%) that was emploied without further purification. (Diastereomeric ratio *Z/E* = 80/20).

^{1}H-NMR, δ: 0.46 (12H, H_a, s); 1.76-1.80 (4H, H_b, m); 2.10-2.25 (4H, H_c, m); 2.35 (6H, H_d, s); 3.98 (4H, H_e, t, J_{eb} = 6.2 Hz); 6.81 (0.4H, H_f, s); 6.93 (1.6H, H_f, s); 7.25 – 7.33 (10H, H_g, m); 7.46-7.50 (2H, H_h, m) ; 7.68-7.85 (2H, H_i, m); 9.32 (0.4H, H_l, s) ; 9.70 (1.6H, H_l, s).

Preparation of (*Z*)-6-chloro-2-[(dimethyl(phenyl)silyl)methylen]hexanal, (*Z*)-6e



5e **2a** **(*Z*)-6e**

Following the general silylformylation procedure, 0.61 mL (4 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.48 mL of 6-Chlorohexyne, **5e**, (d = 0.962 g/mL, 4 mmol), 3 mL of toluene and 0,0030 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up the residue was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 95/5, affording 0.87 g of **(*Z*)-6e** as a pale yellow oil (77 % yield).

^{1}H-NMR, δ: 0.53 (6H, H_a, s); 1.55 – 1.79 (4H, H_b + H_c, m); 2.35 (2H, H_d, dt, J_{db} = 7.6 Hz, J_{df} = 0.6 Hz); 3.53 (2H, H_e, t, J_{ec} = 6.4 Hz); 6.99 (1H, H_f, t, J_{fd} = 0.6 Hz); 7.00 – 7.39 (3H, H_g, m); 7.52 – 7.57 (2H, H_h, m); 9.81 (1H, H_i, s).

^{13}C-NMR, δ: -0.4; 25.4; 30.8; 31.9; 44.4; 127.9; 129.3; 133.3; 137.6; 149.3; 156.1; 192.6.

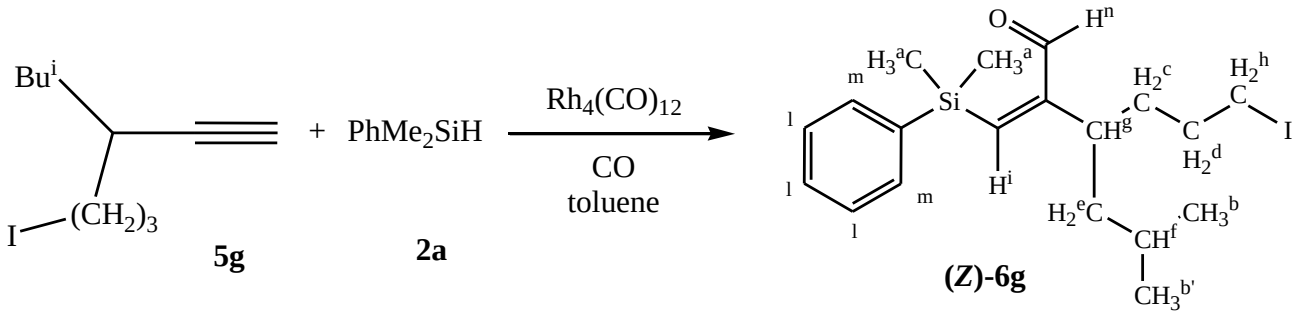
GC-MS, m/z (int. rel. %): 279 (M^+-1, 2); 265 (25); 245 (4); 223 (45); 203 (100); 187 (77); 171 (27); 169 (27); 159 (20); 143 (29); 135 (33); 129 (55); 105 (25); 91 (35); 75 (25); 65 (12); 53 (15); 43 (23).

IR, ν: 2732; 1683; 1588; 1428; 1251; 1112; 835; 731; 698.

Analysis: $C_{15}H_{21}ClOSi$ (280.10)

Calculated	C, 64.14;	H, 7.54;	Cl, 12.62%
Found	C, 64.08;	H, 7.58;	Cl, 12.58%

Preparation of (*R*)(*S*)-(*Z*)-3-(3-iodopropyl)-5-methyl-2-[(dimethyl(phenyl)silyl)methylene]hexanal, (*Z*)-6g



Following the general silylformylation procedure, 0.46 mL (3 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 1.58 g of 3-isobutyl-6-Iodohexyne, **5g**, (6 mmol), 3 mL of toluene and 0,0056 g (0,25 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 50 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 95/5, affording 0.71 g of **(*Z*)-6g** as a pale yellow oil (55% yield).

^{1}H-NMR, δ: 0.57 (6H, H_a, s); 0.90 (3H, H_b, d, J_{bf} = 5.8 Hz); 0.92 (3H, $H_{b'}$, d, $J_{b'f}$ = 5.8 Hz); 1.30-1.73 (7H, H_c + H_d + H_e + H_f, m); 2.92-2.97 (1H, H_g, m); 3.11-3.17 (2H, H_h, m) ; 7.01 (1H, H_i, s); 7.38-7.42 (3H, H_l, m); 7.54-7.59 (2H, H_m, m); 9.86 (1H, H_n, s).

^{13}C-NMR, δ: -0.2; 6.8; 22.0; 23.0; 25.4; 30.9; 35.8; 44.2; 127.9; 129.2; 133.2; 137.6; 148.4; 160.0; 192.4.

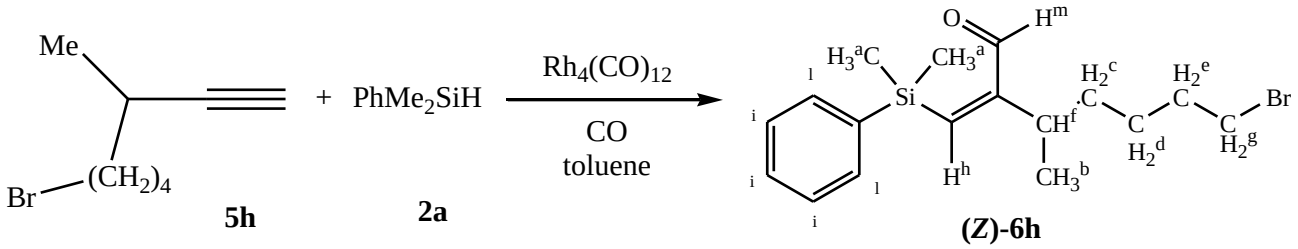
GC-MS, m/z (int. rel. %): 321 (M^+-107, 10); 279 (32); 267 (92); 203 (100); 187 (22); 155 (17); 135 (32); 93 (47); 41 (27).

IR, ν: 2725; 1683; 1585; 1426; 1250; 1114; 839; 821; 732; 698.

Analysis: $C_{19}H_{29}IOSi$ (428.10)

Calculated	C, 53.27;	H, 6.82;	I, 29.62%
Found	C, 53.15;	H, 6.79;	I, 29.71%

Preparation of (*R*)(*S*)-(*Z*)-7-bromo-3-methyl-2-((dimethyl(phenyl)silyl)methylene)heptanal, (*Z*)-6h



Following the general silylformylation procedure, 0.46 mL (3 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.756 g of 3-methyl-7-Bromoheptyne, **5h**, (4 mmol), 3 mL of toluene and 0,0023 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, by a steel siphon, the reactor was pressurized with 40 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the residue was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl ether 80/20, affording 0.85 g of **(*Z*)-6h** as a colorless oil (60% yield).

^{1}H-NMR, δ: 0.50 (6H, H_a, s); 1.03 (3H, H_b, d, J_{bf} = 7.0 Hz); 1.25-1.90 (6H, H_c + H_d + H_e, m); 2.75-2.90 (1H, H_f, m) 3.37 (2H, H_g, t, J_{ge} = 6.8 Hz); 6.90 (1H, H_h, s); 7.34 – 7.37 (3H, H_i, m); 7.47 – 7.52 (2H, H_l, m); 9.76 (1H, H_m, s).

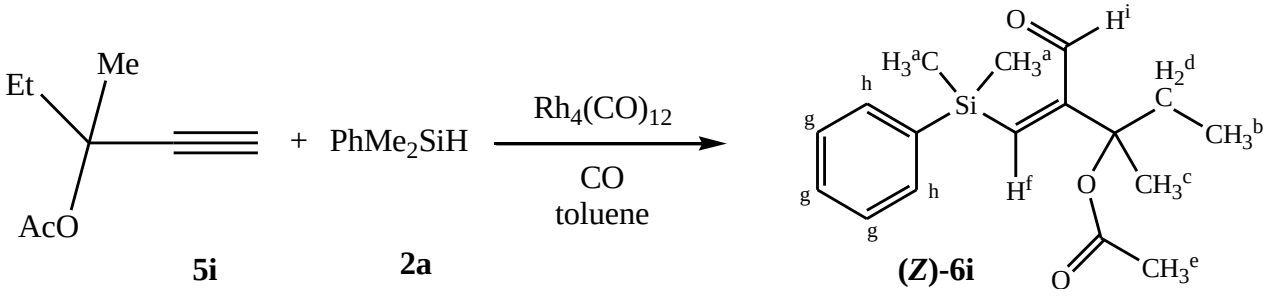
^{13}C-NMR, δ: -0.2; 19.7; 25.6; 32.4; 33.0; 33.6; 34.9; 128.0; 129.3; 133.3; 137.8; 147.1; 161.7; 193.0.

IR, ν: 2728; 1684; 1587; 1427; 1251; 1113; 840; 732; 700.

Analysis: $C_{17}H_{25}BrOSi$ (352.09)

Calculated	C, 57.78;	H, 7.13;	Br, 22.61%
Found	C, 57.85;	H, 7.16;	Br, 22.53%

Preparation of (*Z*)-3-acetoxy-3-methyl-2-((dimethyl(phenyl)silyl)methylene)pentanal, (*Z*)-6i



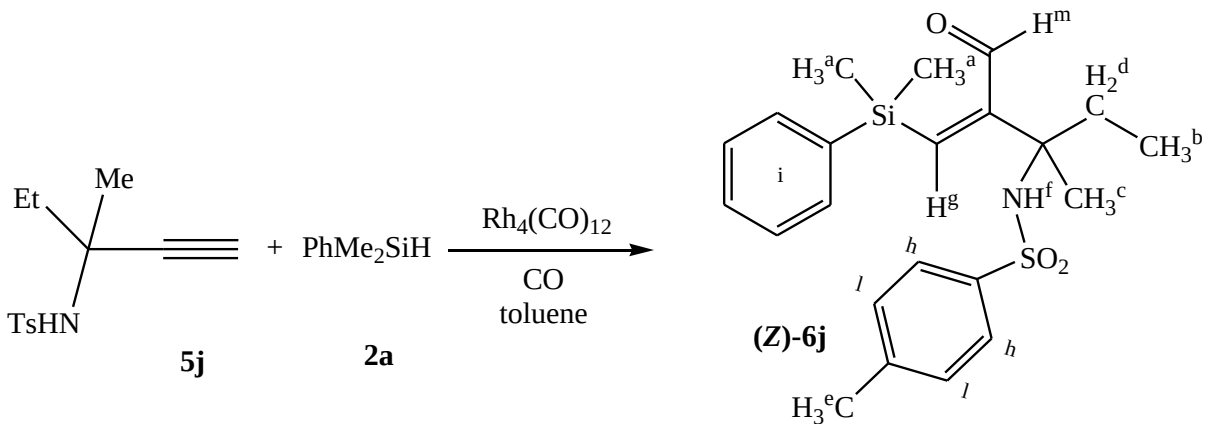
Following the general silylformylation procedure, 0.46 mL (3 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.84 g of 3-Acetoxy-3-Methylbutyne, **5i**, (6 mmol), 3 mL of toluene and 0,0056 g (0,25 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 50 atm of carbon monoxide and the mixture was stirred at room temperature for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with a mixture *n*Hexane/Ethyl acetate 80/20, affording 0.68 g of **(*Z*)-6i** as a colorless oil (75% yield).

^{1}H-NMR, δ: 0.62 (6H, H_a, s); 1.15 (3H, H_b, t, J_{bd} = 7.5 Hz); 1.78 (3H, H_c, s); 1.96-2.08 (2H, H_d, m); 2.13 (3H, H_e, s); 6.99 (1H, H_f, s); 7.47-7.50 (3H, H_g, m); 7.62-7.80 (2H, H_h, m); 9.88 (1H, H_i, s).

Analysis: $C_{17}H_{24}O_3Si$ (304.15)

Calculated	C, 67.06;	H, 7.95%
Found	C, 66.91;	H, 7.96%

Preparation of (Z)-3-methyl-2-[(dimethyl(phenyl)silyl)methylene]-3-(tosylamino)pentanal, (Z) -6j



Following the general silylformylation procedure, 0.31 mL (2 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.50 g of (R)(S)-N-(1-methyl-1-ethyl-2-propinyl)-p-toluensulphonamide, **5j**, (2 mmol), 3 mL of CH_2Cl_2 and 0,0016 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at 100 °C for 24 h. After the usual work up, the crude product was purified by column chromatography on silica gel with dichloromethane, affording 0.37 g of **(*Z*)-6j** as a colorless oil (44% yield).

^{1}H-NMR, δ: 0.48 (6H, H_a, s); 0.80 (3H, H_b, t, J_{bd} = 7.2 Hz); 1.51 (3H, H_c, s); 1.68-1.99 (2H, H_d, m); 2.47 (3H, H_e, s) 5.88 (1H, H_f, s); 6.98 (1H, H_g, s); 7.27 (2H, H_h, d, J_{hl} = 8.2 Hz); 7.45-7.52 (5H, H_i, m); 7.71 (2H, H_l, d, J_{lh} = 8.2 Hz); 9.54 (1H, H_m, s).

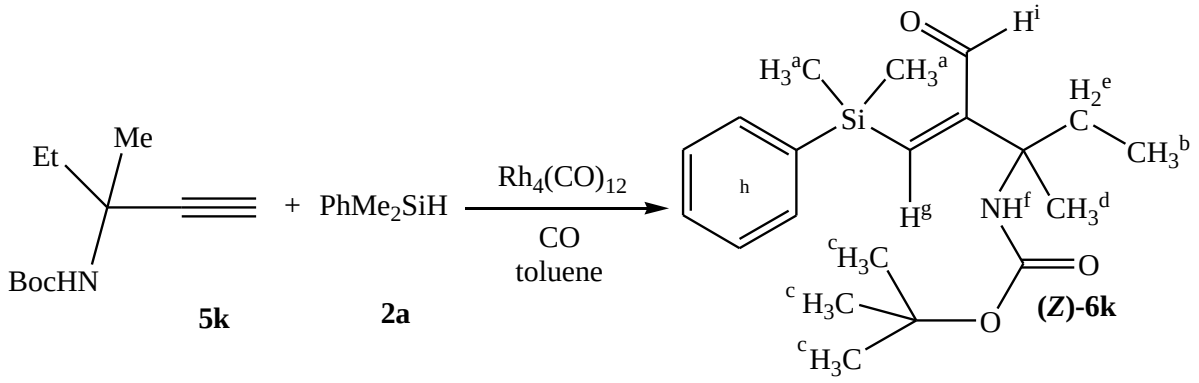
^{13}C-NMR, δ: -0.5; -0.4; 8.1; 21.4; 22.1; 33.9; 61.5; 127.4; 128.2; 129.3; 129.6; 133.4; 137.1; 139.1; 142.9; 151.3; 156.4; 193.1.

IR, ν: 3268; 2965; 2743; 1680; 1597; 1423; 1324; 1250; 1157.

Analysis: $C_{22}H_{29}NO_3SSi$ (415.16)

Calculated	C, 63.58;	H, 7.03;	N, 3.37%
Found	C, 63.71;	H, 7.04;	N, 3.34%

Preparation of (*Z*)-3-methyl-2-[(dimethyl(phenyl)silyl)methylene]-3-(tert-butoxycarbonylamino)pentanal, (*Z*)-6k



Following the general silylformylation procedure, 0.31 mL (2 mmol, d = 0.89 g/mL) of phenyldimethylsilane, **2a,** 0.36 g of 3-methyl-3-N-(ter-butoxycarbonylamino)-1-pentyne, **5k**, (2 mmol), 3 mL of CH_2Cl_2 and 0,0016 g (0,1 mol %) of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave by a steel siphon, the reactor was pressurized with 30 atm of carbon monoxide and the mixture was stirred at 100°C for 4 h. After the usual work up, the crude product was purified by column chromatography on silica gel with dichloromethane, affording 0.45 g of **(*Z*)-6k** as a colorless oil (63% yield).

^{1}H-NMR, δ: 0.62 (6H, H_a, s); 0.76 (3H, H_b, t, J_{bd} = 7.4 Hz); 1.36 (9H, H_c, s); 1.42 (3H, H_d, s); 1.66-1.88 (2H, H_e, m); 6.91 (1H, H_g, s); 7.29-7.54 (5H, H_h, m); 9.75 (1H, H_l, s).

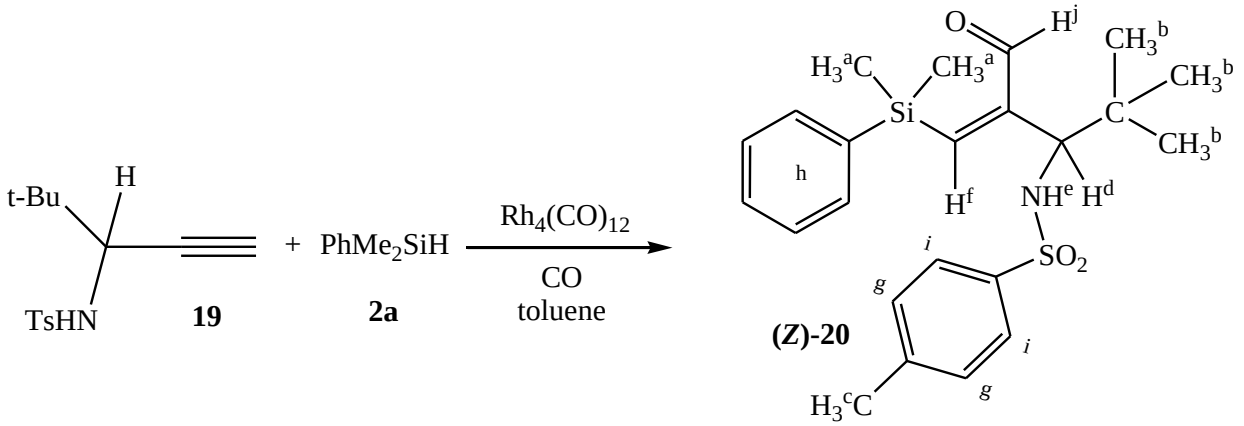
^{13}C-NMR, δ: -0.4; 7.9; 23.7; 28.2; 31.7; 58.3; 79.0; 127.9; 129.2; 133.5; 138.0; 147.7; 154.3; 157.8; 192.5.

IR, ν: 3354; 2972; 2742; 1718; 1694; 1583; 1426; 1250.

Analysis: $C_{20}H_{31}NO_3Si$ (361.21)

Calculated	C, 66.44;	H, 8.64;	N, 3.87%
Found	C, 66.24;	H, 8.66;	N, 3.86%

Preparation of (*Z*)-4,4-dimethyl-2-[(dimethyl(phenyl)silyl)methylene]-3-(tosylamino)pentanal, (*Z*)-20



^{1}H-NMR, δ: 0.30 (3H, H_a, s); 0.31 (3H, H_a, s); 0.83 (9H, H_b, s); 2.36 (3H, H_c, s); 3.92 (1H, H_d, d, J_{de} = 10.0 Hz); 5.80 (1H, H_e, s); 6.72 (1H, H_f, s); 7.16 (2H, H_g, d, J_{gi} = 8.4 Hz); 7.30-7.36 (5H, H_i, m); 7.58 (2H, H_i, d, J_{ig} = 8.4 Hz); 9.36 (1H, H_j, s).

GC-MS, m/z (int. rel. %): 344 (M^+-85, 19); 228 (100); 189 (69); 174 (27); 149 (37); 135 (19); 91; (57); 77(3).

IR, ν: 3277, 2962, 2734, 1687, 1597, 1426, 1322, 1247, 1166.

Analysis: $C_{23}H_{31}NO_3SSi$ (429.18)

Calculated	C, 64.30;	H, 7.27;	N, 3.26%
Found	C, 66.15;	H, 7.30;	N, 3.23%

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